

# Kinetics of Formic acid oxidation on Pt single crystal electrodes modified with Sb adatoms

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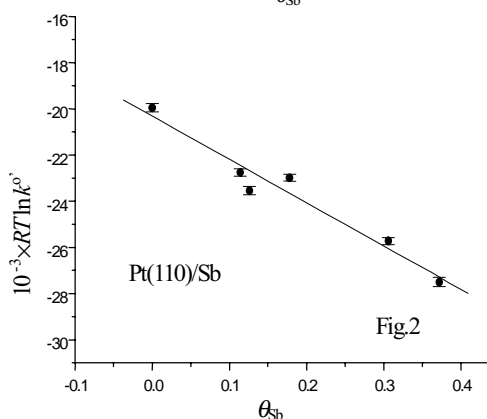
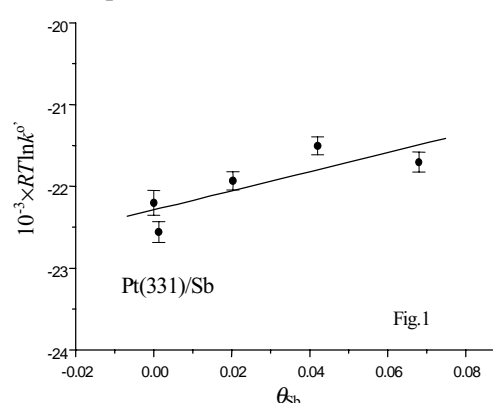
We have studied recently the kinetics of HCOOH electrooxidation on basal planes and stepped surfaces of Pt single crystal (Pt(hkl)) by developing programmed potential step technique and data processing method [1,2], and have determined quantitatively the apparent activation energy that varied with the orientation of Pt single crystal electrode. In the present paper, the kinetics of HCOOH oxidation on Sb adatom modified Pt single crystal electrode (Pt(hkl)/Sb) was further investigated. The rate constant  $k_f$  and the transfer coefficient  $\beta$  were determined on 5 Pt single crystal electrodes (Pt(100), Pt(110), Pt(111), Pt(320) and Pt(331)) modified with irreversibly adsorbed Sb adatoms of different coverages. On the 5 Pt(hkl)/Sb electrodes the amplitude order of  $k_f$  was determined between  $10^{-4}$  and  $10^{-3}$ , and the values of  $\beta$  were all obtained within a range of  $0.10 \pm 0.03$ . The  $\theta_{Sb}$  that yields the highest peak current density of HCOOH oxidation was determined respectively at 0.237 on Pt(100)/Sb, at 0.126 on Pt(110)/Sb, at 0.114 on Pt(111)/Sb, at 0.023 on Pt(320)/Sb and at 0.020 on Pt(331). The results demonstrated: (1) the values of current density  $j$  of HCOOH oxidation on Pt(100), Pt(110) and Pt(320) are all larger than those on Pt(100)/Sb, Pt(110)/Sb and Pt(320)/Sb electrodes. The values of  $j$  on Pt(111) and Pt(331) are nevertheless all smaller than those on Pt(111)/Sb and Pt(331)/Sb electrodes; (2) the potential of current peak ( $E_p$ ) is varied from 0.25 to 0.50V on the 5 bare Pt single crystal electrodes, but it is converged in a narrow range between 0.20V and 0.30V on  $Sb_{ad}$  modified electrodes. The above results imply that the apparent activation energy of HCOOH oxidation has been altered by the presence of Sb adatoms in different way on Pt(hkl) surfaces.

Based on quantitative results we have

proposed, for the first time, a rectifying factor of activation energy ( $\gamma / kJ mol^{-1}$ ) that describes the affecting degree of the activation energy by Sb adatoms. A relationship of  $k_f^{o'} = A \exp[-(\Delta G^{\neq o} + \gamma \theta_{Sb})/RT]$  was introduced to evaluate  $\gamma$ . Fig.1 and Fig.2 illustrated, by taking Pt(110)/Sb and Pt(331)/Sb as examples, the plots of  $RT \ln k^{o'}$  versus  $\theta_{Sb}$ . The  $\gamma$  can be evaluated from the slope of the linear relationship between  $RT \ln k^{o'}$  and  $\theta_{Sb}$ . We have revealed that  $\gamma$  is positive on Pt(100)/Sb, Pt(110)/Sb and Pt(320)/Sb, while it is negative on Pt(111)/Sb and Pt(331)/Sb. The values of  $\gamma$  on the five Pt(hkl)/Sb were determined as  $\gamma_{(100)} = 12.80 \pm 0.317$ ,  $\gamma_{(110)} = 18.74 \pm 0.393$ ,  $\gamma_{(320)} = 16.683 \pm 0.349$ ,  $\gamma_{(111)} = -7.886 \pm 0.288$ ,  $\gamma_{(331)} = -11.69 \pm 0.245$ , respectively. The negative values indicate a decrease of activation energy of HCOOH oxidation by Sb adatoms, which has explained that the  $j$  measured on Pt(111)/Sb and Pt(331)/Sb is larger than the  $j$  acquired on Pt(111) and Pt(331). However, the positive values signify an increase of the activation energy, which has interpreted consequently that the  $j$  measured on Sb modified Pt(hkl) electrodes is smaller than those obtained on bare Pt(hkl) electrodes in cases of Pt(100), Pt(110) and Pt(320).

## References:

1. S.-G. Sun, Y.-Y. Yang, *J. Electroanal. Chem.*, 1999, **467**:121.
2. Y.-Y. Yang, Z.-Y. Zhou, S.-G. Sun, *J. Electroanal. Chem.*, in press



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